

Electropolymerization of Thiophene Derivatives and Composite Materials from Microemulsions

S. Winkels¹, Ch. Stromberg¹, F.-H.Haegel²,
J. Schlüpen², J.W. Schultze¹

¹Institut für Physikalische Chemie und Elektrochemie,
Heinrich-Heine-Universität, Düsseldorf, Germany

²Institut für Chemie und Dynamik der Geosphäre,
Institut 7: Angewandte Physikalische Chemie,
Forschungszentrum Jülich, Germany

Poly-3,4-ethylenedioxythiophene (PEDOT) is a promising material for applications in different technical processes and products. Overoxidation for this polymer is less pronounced and it reveals a high stability and reversibility, e.g. during voltammetric cycling. For this reason PEDOT is already in use for antistatic layers, capacitors and also in the through-hole plating process in printed circuit board fabrication ^[1]. Supplementary, their electronic and ionic conductivity makes composite materials containing platinum group metals applicable for electrocatalysis, e.g. fuel cells ^[2]. Due to the low solubility of the monomer EDOT in water, the electropolymerization of this monomer has been investigated mainly in organic solvents like acetonitrile or propylenecarbonate ^[3]. Nevertheless for the use of EDOT in industrial processes aqueous media are highly favoured. Electropolymerization of EDOT from micellar aqueous solutions with anionic or nonionic surfactants as solvating agents has been reported just recently ^[4,5].

The motivation of this work is to establish microemulsions with low as well as high monomer content to give a more general overview on the feasibility of these solutions as a reaction media for electropolymerization. For this purpose microemulsions have been formulated which consist of the monomer EDOT, an aqueous LiClO₄ solution and a commercial alkyl polyethoxylate (Lutensol® ON110). This pseudoternary system (fig.1) was characterized by phase behaviour, conductivity, viscosity and dynamic light scattering. It shows a transition from the oil-in-water to the bicontinuous microemulsion at an oil content of about 45%. Continuous water domains which are a prerequisite for the electropolymerization exist up to very high oil (EDOT) contents of more than 60% by weight.

The samples for electropolymerization were taken nearby the multiphase region I (series A in fig.1) up to a maximum mass fraction of oil (EDOT) in the binary oil water mixture of $\alpha \sim 80\%$. Anodic electropolymerization of EDOT at a platinum electrode could be carried out from all these microemulsions. The chronoamperograms of electrodeposition reveal that maximum polymerization currents are obtained at about $\alpha = 40\%$ mass fraction of oil (fig.2). To estimate the current efficiency of polymerization and the quality of the deposited PEDOT film, the redox charge Q_{redox} measured during cycling in 0.5M LiClO₄ solution has to be considered. The degree of oxidation γ calculated from the polymerisation charge Q_{pol} and the redox charge Q_{redox} of the film shows that at high polymerization currents and medium oil contents ($20 < \alpha < 60\%$) side reactions like oligomer back diffusion and surfactant degradation dominate the polymerisation. An interesting result is the increase of the degree of oxidation at very high oil contents ($\alpha > 60\%$) up to values of $\gamma = 0.2$ well known for PEDOT films deposited from organic or very diluted

aqueous EDOT solutions (fig.3).

Additional experiments will be carried out from these microemulsion systems to synthesize Pt(Pd)/PEDOT composites. Those composites are expected to show good electrocatalytic properties, e.g. for methanol oxidation or oxygen reduction.

References

1. D. Schattka, S. Winkels, J.W. Schultze, Metalloberfläche, 51 (1997)
2. Z.Qi, M.C.Lefebvre, P.G.Pickup, J. Electroanal. Chem., 459 (1998)
3. H.Randriamahazaka, V.Noël, C.Chevrot, J. Electroanal. Chem., 472 (1999), 103
4. N.Sakmeche, E.A.Bazzaoui, M.Fall, S.Aeiyaach, M.Jouini, J.C.Lacroix, J.J.Aaron, P.C.Lacaze, Synth. Met., 84 (1997), 191
5. V.Tsakova, S.Winkels, J.W.Schultze, Electrochim. Acta, 46 (2000), 759

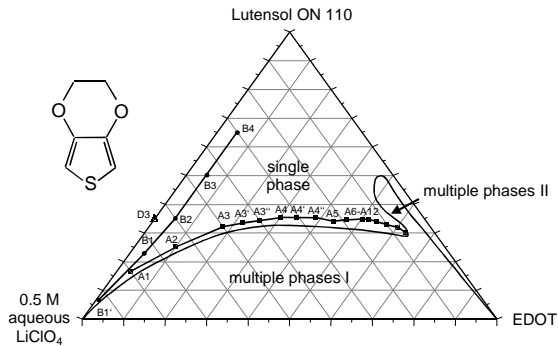


Fig.1 Isothermal phase diagram of the system EDOT / Lutensol® ON110 / 0.5 M LiClO₄ at 25°C

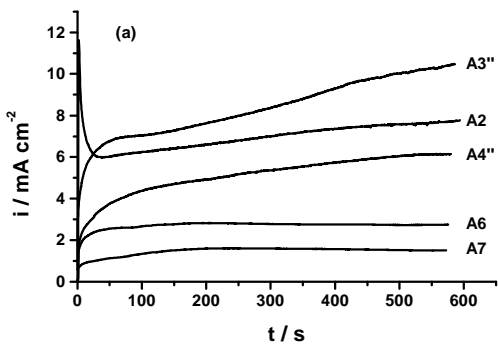


Fig.2 i(t)-curves of polymerization from the microemulsion taken from series A in fig.1

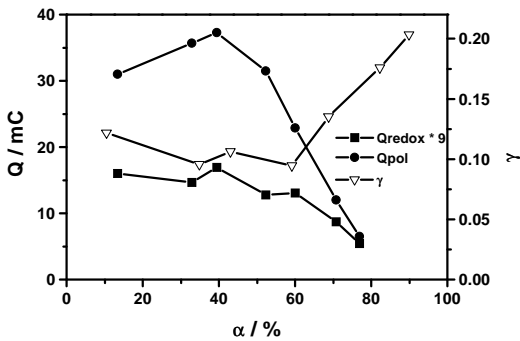


Fig.3 Polymerisation charge Q_{pol} , redox charge Q_{redox} and doping level γ for series A in dependence on mass fraction of oil α